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Effect of oxygen on donor formation in CZ-silicon

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Abstract : Generation of thermal donors (TDs) and oxygen precipitation as a result of low temperature annealing of boron-doped CZ-silicon under nitrogen ambient for different durations has been studied by resistivity and FTIR measurements. Donor generation rate is very rapid in the early stage of annealing and decreases later on. Prolonged annealing accelerates the process of oxygen precipitation yielding a maximum value of 1.97 ppma for 187 hrs of annealing. The oxygen reduction can be described by the second order kinetics. Thermal diffusion coefficient has been estimated to be $\simeq 5.52 \times 10^{-19}$ cm^2 s^{-1} and activation energy 1.089 eV.

CZ-silicon samples with high and moderate oxygen concentrations have also been annealed in air ambient at 450°C and the effect of oxygen and carbon, analysed in all the cases. Ambients do not appear to affect the TD generation kinetics. The results of the influence of oxygen and carbon on donors generated by annealing at 650°C for 100 hrs in the two CZ-Si samples with initial oxygen concentration 33.5 and 34.5 ppma and carbon concentrations 1.5 and 1.0 ppma respectively, and the donors so generated as a function of oxygen carbon reduction due to precipitation are presented and discussed.

Controversial issue of the exact number of oxygen atoms involved in a TD formation is debatable in view of the divergent estimates put-forth by the workers. Involvement of 7–O_i atoms in a single TD sounds more logical as also opined by Lindstrom *et al* [1].

Keywords : Thermal donor, oxygen precipitation, annealing

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1. Introduction

CZ-Si is a starting material for MOS (metal oxide semiconductor) and bipolar process technologies. Oxygen is the most abundant non-intentional impurity incorporated in the melt during growth process from the walls of fused silica crucible. Presence of oxygen $\simeq 2 \times 10^{18}$ cm^{-3} corresponding to the solubility limit of oxygen in silicon at the melting point has been established and is saturated at temperatures needed for device fabrication. Above 300°C oxygen is mobile. Zone refining of silicon in order to reduce oxygen increases material cost significantly. Therefore, supersaturated concentration can be reduced either by out-diffusion or forming complexes or precipitates depending upon the thermal treatment.

Formation of precipitates and of secondary defects is used for internal gettering to remove metallic impurities in the device active region. Heat treatment around 300–500°C yields donor like defects, called thermal donors (TDs) and may be destroyed above 550°C, thereby giving birth to new type of donor called new donors (NDs). The defects so created are electrically active and may affect the performance of a device. Therefore, this problem has been tackled by various workers from different angles still leaving behind a degree of uncertainty over many issues already highlighted on an earlier occasion [2]. The present investigation is aimed to see the effect of oxygen and carbon on donor formation in CZ-silicon.

Various estimates have been put-forth on the exact number of oxygen atoms in the TD formation. KFR model [3] based on electrical, optical and precipitation studies proposed that a TD contains 4 atoms, involvements of more oxygen atoms do not act effectively as donor at room temperature. In OSB model [4], a TD contains 5 or more oxygen atoms with a silicon atom at the centre of cluster, ejection of which terminates the donor activity and brings about stress relaxation. Based on TEM and IR studies Newman [5] suggested that a TD contains 5 oxygen atom on the basis of DLTS (deep-level transient spectroscopy) studies. Mathiot's theoretical kinetic model [6] suggested that a TD contains 3 oxygen atoms assisted by self interstitial, the number of which may vary. Another estimate by Suezawa *et al* [7] based on optical absorption at low temperature, places the number of oxygen atoms participating in TD formation to be 3 to 8. From the above summary, one thing is quite obvious that the exact number of oxygen atoms taking part in TD formation is still uncertain [8].

2. Experimental

2.1. Material :

Czochralski grown boron-doped silicon wafers used for the study of thermal donors, were 400–470 μm thick with 80 mm diameter, as cut, etched, polished surface, <100> orientation and resistivity ranging from 80–100 ohm-cm. These wafers were cut down into small pieces of size 1×2 cm^2 and then subjected to heat treatment in nitrogen ambient, at a constant temperature of 450°C for different durations in the range 1–187 hrs. Wafers from the other region of the same ingot with different oxygen concentration were annealed in air at 450°C. CZ-Wafers used for study of new donors were from different ingot, 600–670 μm in thickness, 80 mm diameter, <100> orientation and both surfaces mirror polished. Two samples referred hereafter as A and B had resistivity values 9.0 and 20.0 ohm-cm and annealed in nitrogen ambient at a constant temperature of 650°C for different duration upto 100 hrs.

2.2. Resistivity measurement and donor generation :

The resistivity of silicon wafer was measured with a collinear four probe array (van der Paw method) at room temperature and the number of carriers derived from Irvin's curve [9]. Afterwards, the wafer was given the desired heat treatment in a nitrogen/air ambient and subsequently cleaned in hydrofluoric acid in order to remove surface oxides. The resistivity

of the annealed samples was again measured and the corresponding number of charge carriers derived from the Irvin's curve. Assuming that the mobility remains constant, the difference of the carrier concentration between un-annealed and annealed samples gives the donors generated or annihilated during the heat treatment.

2.3. Oxygen and precipitated oxygen :

Absorption coefficient needed to compute the oxygen content in the samples has been derived from 1106 cm^{-1} band from FTIR measurements given by Iizuka *et al* [10]. The value of the absorption coefficient α_0 so obtained, was used to calculate the interstitial oxygen concentration using the expression $O_i = (3.3 \pm 0.02) \times 10^{17}\ \alpha_0\ cm^{-3}$. The initial oxygen concentration in the test wafer was measured without any special heat treatment on it. Afterwards, the wafer was given a specific heat treatment and the interstitial oxygen concentration was measured again. The difference between the two is attributed to the precipitated oxygen during heat treatment.

3. Results and discussion

3.1. Annealing in nitrogen ambient at 450°C :

(i) Primary motive of resistivity measurement on the annealed samples has been to ascertain carrier concentration which in turn, helps to find out the donor concentration. Initially, a rapid increase in the value of resistivity is noticed. A further marginal increase in the annealing time causes a sharp fall in the resistivity value and becomes constant at and above 96 hrs of annealing. The numbers of donors generated at 450°C as a function of annealing time leads one to conclude that the generation rate is very rapid in the early stages of annealing and decreases later on. However, longer annealing duration would bring a saturation in the donor concentration. Analysis of the data reveals the formation of two distinct donor species. The maximum donor concentration in our sample is $\simeq 7.9 \times 10^{17}\ cm^{-3}$.

(ii) A smooth and gradual decrease in the values of absorption coefficient as a function of annealing time is observed. The results are in perfect conformity with those reported by Capper *et al* [11]. Oxygen content in the reference sample is $\simeq 5.08 \times 10^{18}\ cm^{-3}$ which got reduced to a minimum $\simeq 4.09 \times 10^{18}\ cm^{-3}$ in sample annealed for 187 hrs [12].

(iii) Prolonged annealing times accelerate the process of oxygen precipitation, so is the case with the donor formation which is a perspicuous expectation. The maximum oxygen precipitation observed in our samples was $\simeq 1.97$ ppma.

(iv) A simple plot of the differences of the reciprocal values of the actual and initial oxygen concentration $[C(t)^{-1} - Co^{-1}]$ as a function of annealing time at 450°C yields a straight line suggesting that the oxygen reduction can be described by second order kinetics [13]. From the gradient of the straight line equal to $8\pi DR$, the diffusion coefficient D has been determined to be $\simeq 5.52 \times 10^{-19}\ cm^2\ s^{-1}$ where R means the distance at which two oxygen atoms bind together to form a complex. $R = 5.0 \times 10^{-8}$ cm has been used in the above calculation [5]. The value of D so obtained is substituted in the expression $D = 0.17$

exp ($-E/kT$) $cm^2\ s^{-1}$ which yields the value of activation energy to be 1.089 eV. Even lower activation energy as compared to the above value for oxygen diffusion, *i.e.* $E_D = (0.7 \pm 0.2)$ eV was found by Gaworzewski and Schmalz [14] for annealing at temperatures between 525 and 600°C. This lower activation energy can be explained by sinks of diffused oxygen. This may also be due to the interactions of the diffused oxygen with other species of self-interstitials having sufficiently high diffusivity at these temperatures.

3.2. Annealing in air ambient at 450°C :

This study has been carried out to ascertain whether ambients affect the donor formation and oxygen precipitation or not. The wafers were taken from the same ingot but with different oxygen and carbon contents. The results for the samples annealed in air-ambient are almost parallel to those reported in Section 3.1 and the difference in the values of donors generated and oxygen precipitated is due to the different initial oxygen and carbon contents in the parent samples. This result is in tune with the finding reported by Bean and Newman [15] who suggested that the ambient atmosphere, whether this was wet or dry vacuum, hydrogen or deuterium did not affect the results.

A few other important results are as follows :

1. Annealing of the samples for longer time, helps us to remove the inhomogeneities present in the sample upto a greater extent as may be inferred from resistivity measurements.
2. There is increase in the ρ-values upto 1 hr. After that, there is a sharp fall in the ρ-values as a function of annealing time and tends to a constant value above 55 hrs.
3. The rate of donors generated is very rapid in the early stage of annealing but later on the donor generation rate decreases. The maximum donor concentration obtained in our sample is $\simeq 1.79 \times 10^{17}\ cm^{-3}$.
4. A continuous and gradual decrease in absorption coefficient has been noticed as a function of annealing time. The calculated oxygen and carbon concentrations in unannealed (reference) sample is $\simeq 1.27 \times 10^{18}\ cm^{-3}$ and $\simeq 7.66 \times 10^{17}\ cm^{-3}$ respectively. The initial carbon concentration in the second group of samples (higher carbon and oxygen content samples) is $\simeq 1.18 \times 10^{17}\ cm^{-3}$.
5. The oxygen and carbon concentrations in samples annealed for 55 hrs are $\simeq 1.15 \times 10^{18}\ cm^{-3}$ and $\simeq 7.11 \times 10^{17}\ cm^{-3}$ respectively. In the second group of samples, the minimum carbon concentration for 55 hrs is $\simeq 1.06 \times 10^{18}\ cm^{-3}$.
6. The maximum oxygen and carbon precipitation observed in our sample is $\simeq 2.362$ ppma and $\simeq 1.100$ ppma and in the second group of samples (containing higher oxygen and carbon concentration) the maximum oxygen precipitation observed is 2.310 ppma.
7. The oxygen reduction can be described by the second order kinetics. The thermal diffusion coefficient of oxygen comes out to be $4.17 \times 10^{-19}\ cm^2\ s^{-1}$ and activation energy 0.823 eV.

3.3. Annealing in nitrogen ambient at 650°C :

The donor generation by the annealing at 650°C for different durations is plotted in Figure 1 which clearly shows that the donor generation is very fast and saturates at 75 hrs of annealing. Carbon and oxygen precipitation in terms of change in the carbon and oxygen concentrations as a function of annealing time is shown in Figure 2. This shows that the donor generation depends on both carbon and oxygen concentration.

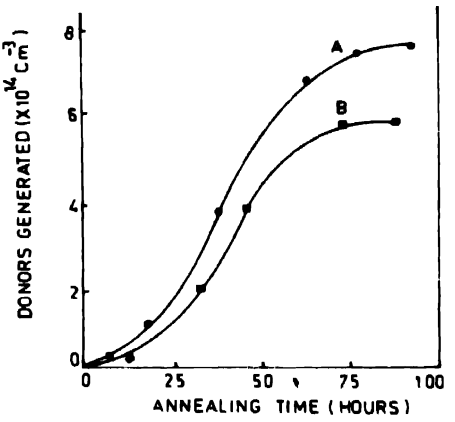

Figure 1. Donor concentration as a function of annealing time by annealing at 650°C.

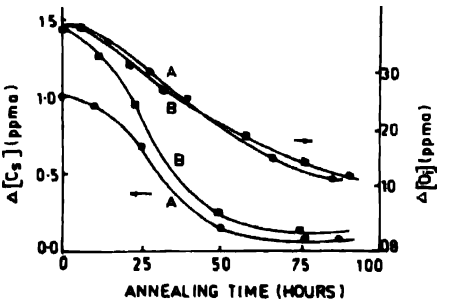

Figure 2. Change in carbon and oxygen concentration as a function of annealing time by annealing at 650°C.

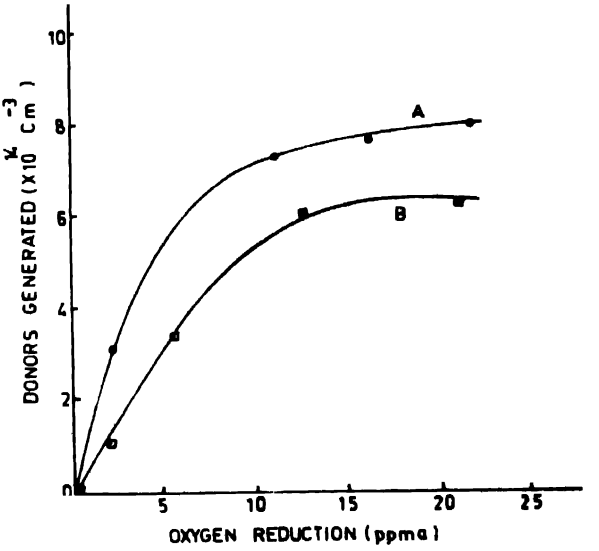

Figure 3. Donor concentration and oxygen reduction by annealing at 650°C.

Donors generated has been correlated with the oxygen reduction as shown in Figure 3. It is clear from the figure that carbon enhances the donor formation which is

higher in the sample with less carbon concentration. Donors generated versus carbon reduction have been plotted in Figure 4. Steep-rise in the donors generated may clearly be

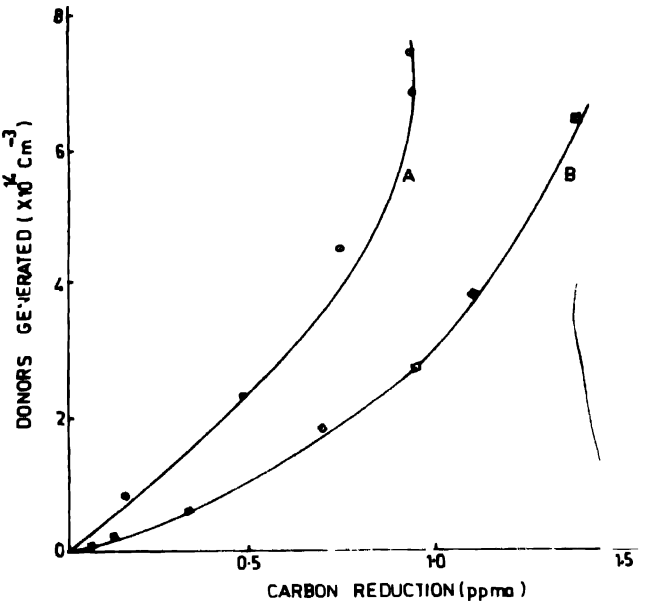

Figure 4. Donor concentration and carbon reduction by annealing at 650°C.

attributed to the saturation of carbon reduction. The graphs are self-explanatory and the results agree with those reported by Ohsawa *et al* [16].

4. Some numerical estimates of the O-atoms in the TD formation

Logically, involvement of 7 O_i atoms in a single TD sounds more reasonable as also opined by Lindstrom *et al* [1] because thermal treatment creates a silicon self interstitial (Si_i) and Si_i so created is surrounded by six O_i-atoms which become more mobile as a result of an increase in temperature. One O_i occupies the site vacated by silicon atom. One single TD may contain seven nearest O_i atoms with Si as nucleus [17].

5. Summary

1. Annealing of the wafers under different ambients whether nitrogen or air, does not have any influence on the behaviour of the parameters calculated. Whatsoever difference we observe, is attributable to the presence of initial oxygen and carbon concentrations in the incoming wafers.
2. Oxygen reduction can be described by the second order kinetics.
3. There is the involvement of 7 O_i atoms in a single TD.
4. Carbon suppresses the thermal donor formation.

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